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Preparation of porous alumina/ceria composite abrasive and its chemical mechanical polishing behavior

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A porous alumina/ceria composite abrasive is synthesized by the hydrothermal synthesis method with transmission electron microscope images showing that it has wormhole-like pores. The chemical mechanical polishing performance of the synthesized abrasive on hard disk substrates was then investigated and the results showed that, compared with pure porous alumina and solid alumina, the porous alumina/ceria composite abrasive has a higher material removal rate because of the presence of the active polishing element cerium. Also, the surfaces polished by the porous alumina abrasives had much fewer topographical variations and a lower surface roughness than those polished by solid alumina abrasive. © *2013 American Vacuum Society*.
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I. INTRODUCTION

With the increasing capacity of the hard disk, enhanced rotational speed, and the decreasing distance between the magnetic head and substrate, higher requirements are being set for a hard disk substrate to minimize roughness and defects on the polished surface.

At present, chemical mechanical polishing (CMP) is the only technology known to provide global planarization of the topography with a low postplanarization slope.[1–4]

In CMP, the abrasive is one of the key influencing factors on the polished surface quality. Its properties, such as particle type, size, shape, and concentration, play an important role in determining the optimum CMP performance.[5] Traditional inorganic abrasives, such as alumina,[6,7] silica,[8] and ceria,[9–11] have been widely used in CMP slurries, but these abrasives are all compact solid particles and often lead to undesired CMP performance because of their high hardness values.

Recently, porous materials as abrasives have attracted a great deal of attention due to the channel structure, high surface area, and uniform pore size. Their special pore channel structure could reduce the hardness of the abrasives in that, after polishing by a slurry containing porous silica abrasive, a smoother surface with less scratching was obtained than with compact solid particles.[12,13] Furthermore, cerium-incorporated porous silica composite abrasives with larger pores[14] showed a better CMP performance than porous silica.

Alumina is also a widely used CMP abrasive, but it has higher hardness and is easier to agglomerate than silica which often leads to more surface defects. In our previous work, Wu *et al.*[15] prepared porous alumina abrasives which produced a better polished surface than the solid alumina abrasives. Ceria nanoparticles are a key abrasive nanomaterial used for CMP of advanced integrated circuits; however, ceria nanoparticles synthesized by the existing techniques are irregularly faceted, causing scratching on the wafers and increase defect concentrations.[16] Thus, a cerium-incorporated porous alumina composite abrasive may also have a better CMP performance than solid alumina and porous alumina.

Up to now, cerium-incorporated porous alumina abrasive used in CMP slurries has seldom been reported. In the present paper, cerium as an active polishing element, which can catalyze dissociation of peroxide,[17,18] incorporated into a porous alumina abrasive has been synthesized by the hydrothermal synthesis method. In addition, the CMP performance of solid alumina, porous alumina, and porous alumina/ceria abrasives on hard disks has been investigated.

II. EXPERIMENT

A. Preparation of the porous alumina/ceria abrasive

The porous alumina/ceria abrasive was prepared using the hydrothermal synthesis method.[19] Sodium dodecyl sulphate (SDS) was used as a polymeric template, and 150 g of $Al(NO_3)_3{\cdot}9H_2O$ and 17.2 g of $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in 200 ml deionized water and then mixed with 200 ml of 2 mol/l ammonia solution. The *p*H value of the aluminum nitrate solution was 2.68 after the addition of ammonia. Then, 72 g of urea and 28.8 g of SDS were added to the above solution while being stirred, and the resulting homogeneous solution was put into a sealed Teflon-lined stainless autoclave vessel for static hydrothermal reaction at 100 °C for 48 h. After the reaction process, the resulting pale yellow precipitate was recovered by centrifugation, washed with deionized water several times, and dried at 110 °C for 12 h. Calcination was carried out by slowly increasing the temperature from room temperature to 800 °C (1 °C min^{-1} ramping rate) and by heating at 800 °C for 4 h in air.

Porous alumina and solid alumina abrasives were also prepared as comparisons in the CMP test. Porous alumina[19] and solid alumina abrasives were synthesized by a similar method to the one described above, though for the synthesis of porous alumina $Ce(NO_3)_3{\cdot}6H_2O$ was not added, and for the synthesis of solid alumina $Ce(NO_3)_3{\cdot}6H_2O$ and SDS were not added.

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B. Characterization of the porous alumina abrasive

Transmission electron microscopy (TEM) images were obtained by a JEOL 2000 CX electron microscope operating at an accelerating voltage of 200 kV, where the samples were ultrasonically dispersed in ethanol and then dropped onto the carbon-coated copper grids prior to the observation.

Particle size was determined using a Malvern Zetasizer 3000HS laser particle size analyzer with a measuring range of 2 to 3000 nm.

Elementary analysis of the sample was obtained by cold field emission SEM (JSM-6700F) with the expanded functionality of an embedded energy dispersive spectrometer (EDS) and a resolution is at $Mn_{Ka} < 136$ eV. The EDS was constructed by the British OXFORD Company.

The effect of the prepared porous alumina/ceria abrasive upon the concentration of the free radical in H_2O_2 was measured by EMX–electron paramagnetic resonance (EPR) (Center field: 3518.07 G, scan width: 100 G, microwave power: 20 mW, scan time: 5.24 s, scanning frequency: 6 times), and dimethyl pyridine N-oxide (DMPO) was added as a trapping agent. Preparation of the sample for the EPR test was as follows: 2.725 g of porous alumina/ceria was added to 47.275 g deionized water and dispersed for 15 min by ultrasonic, after which 3.003 g of 30 wt. % H_2O_2 was added, shaking well. After resting for 4 h, 40 μl of the obtained sample was mixed with 10 μl of 0.5 mol/l DMPO and stirred quickly for the EPR test.

C. Preparation of the porous alumina/ceria slurry, porous alumina slurry, and solid alumina slurry

The preparations of the alumina/ceria slurry, porous alumina slurry, and solid alumina slurry all have the same process. First, 3.64 wt. % prepared abrasives and 5.45 wt. % functional additives were added into deionized water in a container while continuously stirring. Second, the mixture was milled for 4 h in a vibrator containing ZrO_2 milling balls. After milling, the average diameter of the porous alumina/ceria abrasive is found to be 327 nm, the average diameter of porous alumina is 323 nm, and the average diameter of the solid alumina is 300 nm. Third, the mixture was filtrated with a 10 μm pore filter and, fourth and last, 7.28 wt. % H_2O_2 as oxidant was added to the mixture to obtain the slurry.

D. Polishing tests

Polishing tests were performed with UNIPOL-1502 polishing equipment made by Shenyang Kejing Instrument, Co. Ltd, China, using as workpieces hard disks with Φ95 mm $\times$ 1.25 mm (a center hole with $\Phi = 25$ mm) aluminum alloy substrates plated with NiP, which consists of about 85 wt. % nickel and 15 wt. % phosphorus elements with an average roughness (Ra) of about 40 nm (Shenzhen Kaifa Magnetic Recording Company, China). The polishing pad used is a DPC5150 Rodel porous polyurethane pad, and the polishing conditions are as follows: the down force is varied from 1 to 5 kg, the rotation speed is varied from 20 to 80 rpm, the polishing time is 30 min, and the slurry supplying rate is 167 ml/min. After polishing, the hard disk substrates were washed using ultrasonic in a cleaning solution containing 0.5 wt. % surfactant (polyoxyethylene alkyl ether) in deionized water and dried in a dry oven.

E. Examination of the polished surfaces

The surface Ra and material removal rate (MRR) were measured to evaluate the polishing effects under different polishing conditions. The Ra and polishing surface topography was measured by an Ambios XI-100 surface profiler (Ambios Technology Corp., USA, ZYGO) with a vertical resolution of 0.1 Å in Texture Modes and the measuring area of 500 μm $\times$ 500 μm. The depth of focus is 3.0 μm, the working distance is 7.4 mm, and the numerical aperture is 0.30.

The mass of the hard disk substrate was measured by an analytical balance and all data are the mean values of four tests.

III. RESULTS AND DISCUSSION

A. EDS of the porous alumina/ceria abrasive

A spectrum of the energy versus relative counts of the detected x rays is obtained and evaluated for qualitative and quantitative determination of the elements present.[20] From Fig. 1, it is seen that the ceria has been incorporated into the abrasive. Elemental composition mapping acquired by the EDS system shows a rather uniform distribution of Al and Ce in the sample studied, with a small amount of S (originating from the template) for the samples calcined at 800 °C.[21] According to the analysis of Table I, the atom ratio of Al and Ce in the synthetic abrasive is 9:1.

B. TEM of the alumina/ceria abrasive

Figure 2(a) shows a TEM image of the porous alumina/ceria which has wormhole-like pores similar to that of pure porous alumina [Fig. 2(b)].[22] As shown in Fig. 2(c),[23] there is no porous structure in the case of solid alumina. By comparison with porous alumina [Fig. 2(b)], the particles and clusters containing ceria species on the surface are not observed in the TEM image of porous alumina/ceria [Fig. 2(a)].

Normally, if the ceria clusters cannot be observed on the external surface from the TEM image, according to the

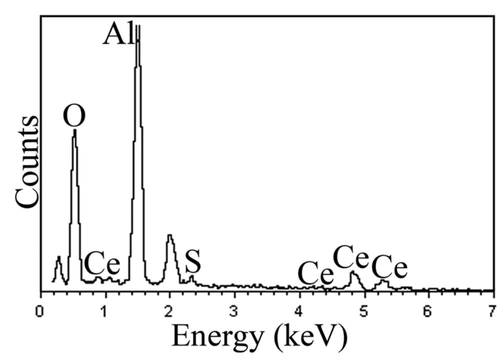

FIG. 1. EDS spectra of the porous alumina/ceria abrasive.

TABLE I. EDS spectra analysis of the porous alumina/ceria abrasive.

Element	Weight ratio	Atom ratio
O	37.7	58.97
Al	38.38	35.60
S	1.93	1.50
Ce	21.99	3.93
Total	100.00	100.00

elemental composition mapping evidence, they may be believed to be inside spaces;[23] therefore, we can conclude that the ceria species to some degree have incorporated into the framework of the alumina abrasive.

C. Electron paramagnetic resonance test of the H_2O_2 with porous alumina/ceria abrasive

In order to find out the effect of Ce in the CMP process, the EPR test was performed, and the electron spin resonance spectra of H_2O_2 and H_2O_2 with the porous alumina/ceria abrasive are shown in Figs. 3(a) and 3(b), respectively. The spectra in Figs. 3(c) and 3(d) are typical of the DMPO-O_2^- free radical and the DMPO-OH· free radical, respectively.[24,25] It is found that the spectra of H_2O_2 with the porous alumina/ceria abrasive exhibit both DMPO-O_2^- and DMPO-OH· free radicals, but the spectra of just H_2O_2 shows that only the DMPO-OH· free radical exists. Also, the intensity of the DMPO-OH· free radical with porous alumina/ceria abrasive is much larger than that without the abrasive. In other words, the free radical concentration of H_2O_2 with the porous alumina/ceria abrasive is much larger than that of H_2O_2 without the abrasive, so it can be inferred that the incorporation of Ce strongly catalyses H_2O_2 decomposition into OH· and ·O_2^-, which could accelerate chemical etching during the CMP process. The decomposition mechanisms of H_2O_2 with the porous alumina/ceria abrasive may be similar to the Radical Mechanism of Choudhary and Samanta[26,27] and are proposed in Table II.

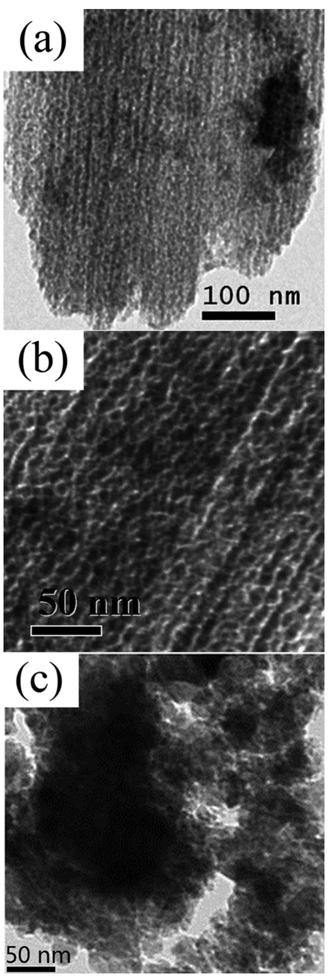

FIG. 2. TEM image of (a) porous alumina/ceria (Ce molar fraction: 10%), (b) porous alumina, and (c) solid alumina.

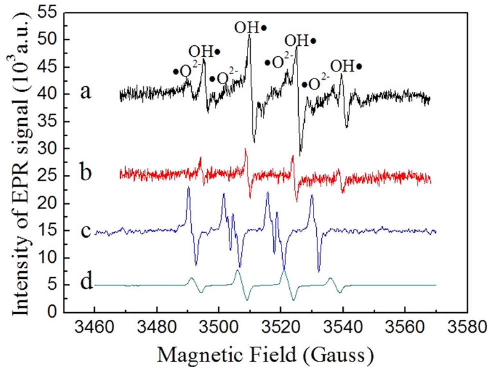

FIG. 3. (Color online) Electron spin resonance spectra of (a) H_2O_2 with porous alumina/ceria abrasive, (b) H_2O_2, (c) DMPO-O_2^- free radical, and (d) DMPO-OH· free radical.

D. CMP performance of the slurries

Figure 4 shows the effects of the rotation speed and down force upon the MRR of the hard disk substrate. With increasing down force or rotation speed, the MRR of the hard disk substrate separately polished by the three slurries (solid alumina, porous alumina, and porous alumina/ceria abrasives) increases gradually. The increased rotation speed gives more chances for friction between the hard disk substrate and the polishing pad and abrasives, while a greater down force gives a stronger mechanical grinding effect in order to impact and grind the substrate surface.[28]

Furthermore, the MRR of hard disk substrates polished by the porous alumina/ceria slurry is much larger than those polished by the porous alumina and solid alumina slurries. The increase of the MRR here may be attributed to the existence of the active polishing element (Ce), which could accelerate chemical etching due to the fact that the incorporated Ce strongly catalyzes the H_2O_2 decomposition into the strong oxidative free radicals OH· and ·O_2^-, according to the above EPR analysis.

Figure 5 shows the effects of the rotation speed and the down force on the Ra of the hard disk substrates. It can be seen that with increasing rotation speed and down force, the Ra of the hard disk substrates decreases gradually at first and then increases when rotation speed is over 60 rpm or the down force is over 4 kg. Considering that there are many

TABLE II. Decomposition mechanisms of H_2O_2 with porous alumina/ceria abrasive * denotes Ce catalytic site.[a]

Step	Limiting rate expression	Rate expression number
(1) $2H_2O_2 + 4^* \rightarrow 4^*OH$	$r = k_1 C_{H2O2}^2/\{1 + (K_3 C_{O2})^{1/2} + C_{H2O}^{1/2}[(K_3/K_2)C_{O2}]^{1/4}\}^4$	1
(2) $4^*OH \rightarrow 2H_2O + 2^*O + 2^*$	$r = k_2/[(1/K_1^{1/4} C_{H2O2}^{1/2}) + (1/K_1^{1/4})(C_{O2}/K_3 C_{H2O2})^{1/2} + 1]^4$	2
(3) $2^*O \rightarrow O_2 + 2^*$	$r = k_3/\{1 + [C_{H2O}/(K_1 K_2)^{1/2} C_{H2O2}] + [C_{H2O}/K_1^{1/4} K_2^{1/2} C_{H2O2}^{1/2}]\}^2$	3
(4) $O_2 + e^- \rightarrow {}^*O_2^-$		4

[a]Parameters k_i and K_i are the rate constants and equilibrium coefficients, respectively, that correspond to step i of a mechanism.

rough peaks on the surface of substrates initially, during the polishing process, these rough peaks would be removed, and with an increase of the down force or rotation speed, the removal of the rough peaks might increase, too. However, if the down force or rotation speed is increased too much, it might cause some surface defects or deformations, leading to the increase of the Ra. From Figs. 5(a) and 5(b), we can find that the optimum conditions for hard disk substrate CMP are that of a rotation speed of about 60 rpm and a down force of about 4 kg, considering the Ra.

In addition, the Ra of the hard disk substrate polished by the solid alumina slurry is much larger than those polished by the porous alumina and porous alumina/ceria slurries. The improvement of the Ra may be attributed to the porous structure which reduces the hardness of abrasives and, because of its moderate hardness, the porous alumina and porous alumina/ceria showed suitable mechanical action. In addition, the porous structures would not cause large surface scratches and other defects and, thus, demonstrate good polishing performance.

Further, in order to investigate the difference in the polishing performance between solid alumina, porous alumina, and porous alumina/ceria abrasives, the topographical micrographs of polished hard disk substrate surfaces were analyzed by an AMBIOS TECHNOLOGY XI-100 Optical Surface Profiler, with the results shown in Fig. 6. These results show that the surface before polishing is very rough with the periodic topography or scratches from the before grinding process, and with a Ra of 49.25 nm. After polishing in the slurry containing solid alumina abrasive, the surface became smooth (Ra = 18.08 nm), but some small scratches

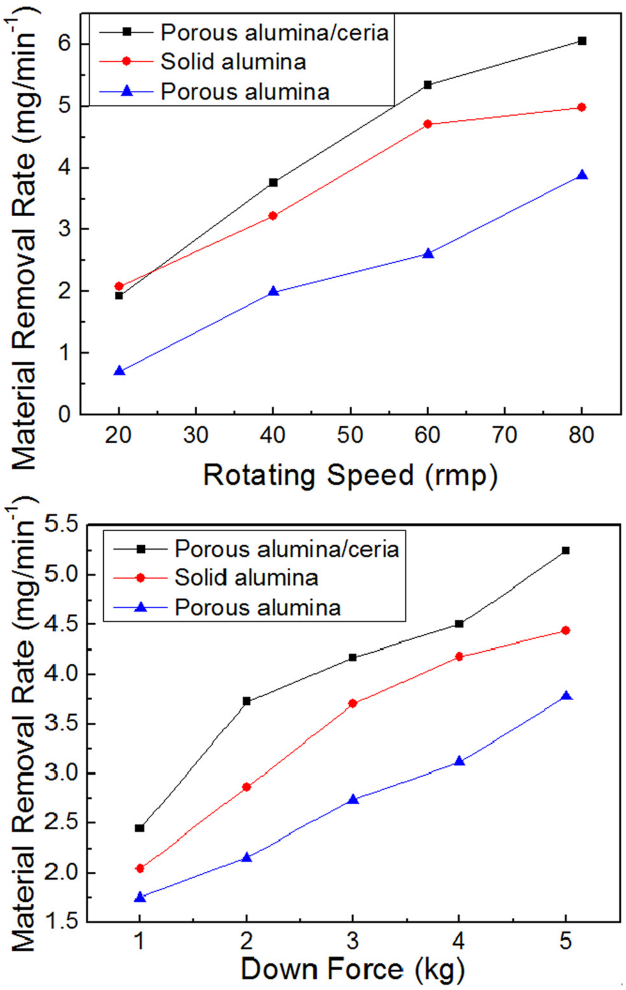

FIG. 4. (Color online) (a) Effect of rotation speed on MRR (polishing condition: down force of 4 kg and polishing time of 30 min). (b) The effect of down force on MRR (polishing conditions: rotation speed of 60 rpm and polishing time of 30 min).

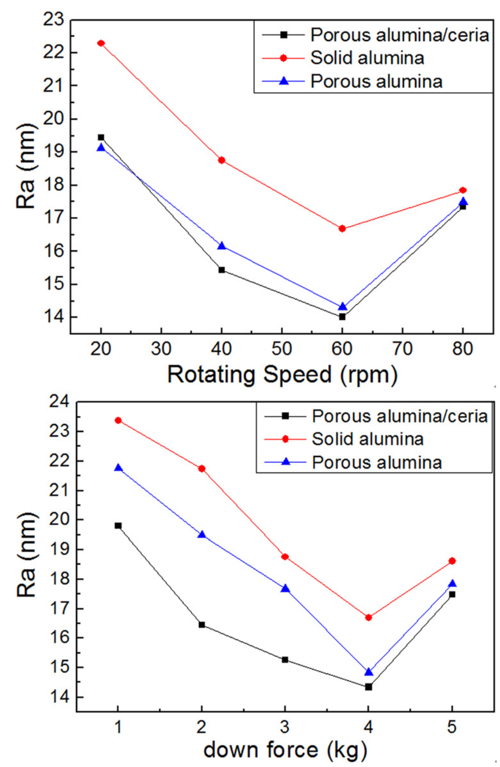

FIG. 5. (Color online) (a) Effect of rotation speed on Ra (polishing conditions were down force of 4 kg and polishing time of 30 min). (b) The effect of down force on Ra (polishing conditions were rotation speed of 60 rpm and polishing time of 30 min).

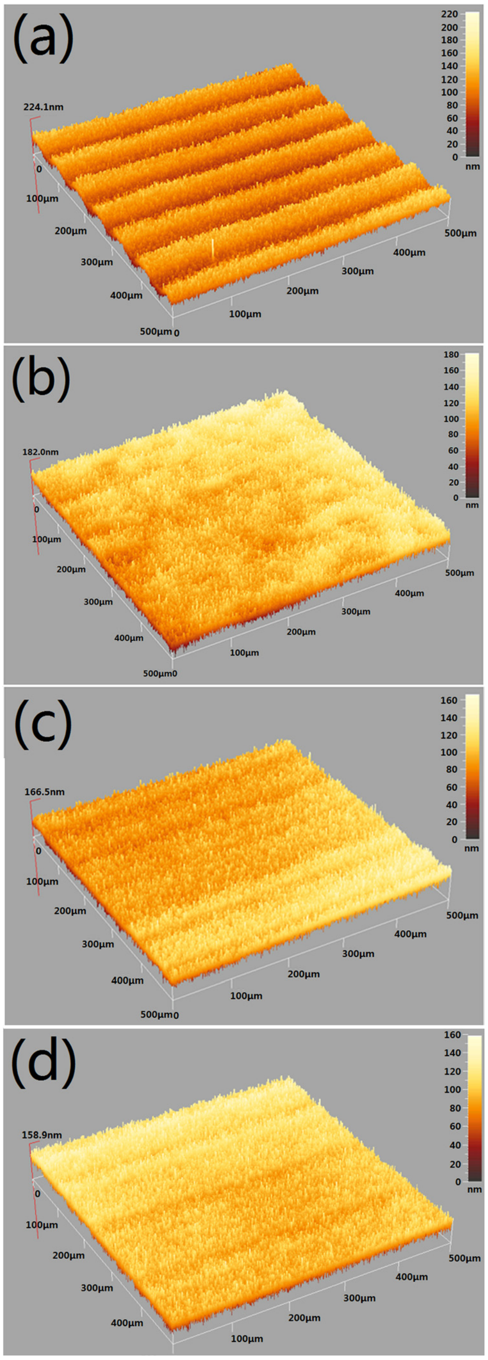

FIG. 6. (Color online) Surface profiles of hard disk substrates (a) before polishing, Ra = 49.25 nm (Ref. 20); (b) polished by the solid alumina slurry, Ra = 18.08 nm (Ref. 20); (c) polished by the porous alumina slurry, Ra = 14.30 nm (Ref. 20); (d) polished by porous alumina/ceria slurry, Ra = 14.01 nm (polishing conditions were rotation speed of 60 rpm, down force of 4 kg and polishing time of 30 min).

still exists there. However, when polished with slurry containing porous alumina and porous alumina/ceria abrasives under the same polishing conditions, the surface becomes smoother (Ra of 14.30 and 14.01 nm, respectively) and the scratches can scarcely be observed. The lower Ra value means a higher surface planarization, meaning that the prepared porous alumina and porous alumina/ceria abrasives possess higher surface planarization than the solid alumina abrasive. This may be attributed to the porous structure which reduces the hardness of the abrasives and which this will result in fewer surface scratches and other defects.

IV. SUMMARY AND CONCLUSIONS

An alumina/ceria composite abrasive with wormhole-like pores is synthesized by the hydrothermal synthesis method.

In hard disk CMP, compared with solid alumina and porous alumina abrasives, the prepared porous alumina/ceria abrasive has a higher MRR which can be attributed to the active polishing element Ce incorporated in the alumina abrasive which is able to strongly catalyze the decomposing of H_2O_2 into the $-OH\cdot$ and $\cdot O_2^-$ free radicals. These free radicals have strong oxidizability and can accelerate chemical etching during the CMP process.

The surfaces of the hard disk polished by the porous alumina and porous alumina/ceria abrasives have much lower topographical variations and surface roughness (Ra) than those polished by the solid alumina abrasive because they have lower hardness and good adsorption.

These results imply that the porous alumina/ceria abrasive possesses good surface polishing performance and promising prospects in CMP.

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[1]F. Malik and M. Hasan, Thin Solid Films **270**, 612 (1995).
[2]H. Lei and J. Luo, Wear **257**, 461 (2004).
[3]H. Lei, J. Luo, and L. Xinchun, Mech. Eng. **19**, 496 (2006).
[4]H. Lei, N. Bu, R. Chen, and P. Hao, Thin Solid Films **518**, 3792 (2010).
[5]R. Carpio, J. Farkas, and R. Jairath, Thin Solid Films **266**, 238 (1995).
[6]H. Lei, Y. Chu, and X. Tu, J. Funct. Mater. **36**, 1425 (2005) (in Chinese).
[7]X. Wang, X. Meng, and D. Liu, Lubr. Eng. **32**, 38 (2007) (in Chinese).
[8]H. Lei, P. Zhang, and H. Lu, Lubr. Eng. **173**, 31 (2006) (in Chinese).
[9]L. Wang, K. Zhang, Z. Song, and S. Feng, Appl. Surf. Sci. **253**, 4951 (2007).
[10]S. Robert and S. Harrie, Mach. Sci. Technol. **4**, 235 (2000).
[11]I. Tetsuro, Lubr. Eng. **33**, 267 (1998) (in Chinese).
[12]P. Liu, H. Lei, and R. Chen, Int. J. Abrasive Technol. **3**, 228 (2010).
[13]H. Lei, H. Li, P. Liu, and R. Chen, Am. J. Nanotechnol. **1**, 32 (2010).
[14]P. Hao, H. Lei, and R. Chen, Int. J. Abrasive Technol. **4**, 255 (2011).
[15]X. Wu, H. Lei, and R. Chen, Adv. Mater. Res. **338**, 415 (2011).
[16]X. Feng *et al.*, Science **312**, 1504 (2006).
[17]A. Hiroki and J. A. LaVerne, J. Phys. Chem. B **109**, 3364 (2005).
[18]E. Aneggi, V. Cabbai, A. Trovarelli, and D. Goi, Int. J. Photoenergy **2012**, 1 (2012).
[19]Q. Liu, A. Wang, X. Wang, and T. Zhang, Microporous Mesoporous Mater. **100**, 35 (2007).
[20]A. Argast and F. C. Tennis, J. Geosci. Educ. **52**, 213 (2004).
[21]S. M. Morris, J. A. Horton, and M. Jaroniec, Microporous Mater. **128**, 180 (2010).
[22]H. Lei, X. Wu, and R. Chen, Thin Solid Films **520**, 2868 (2012).
[23]H. Lei, L. Jiang, and R. Chen, Powder Technol. **219**, 99 (2012).
[24]Z. Cheng, H. Zhou, J. Yin, and L. Yu, J. Agric. Food Chem. **55**, 3325 (2007).
[25]G. R. Buettner, Free Radical Res. **10**, 11 (1990).
[26]Y. Voloshin, J. Manganaro, and A. Lawal, Ind. Eng. Chem. Res. **47**, 8119 (2008).
[27]R. V. Choudhary and C. Samanta, J. Catal. **238**, 28 (2006).
[28]L. M. Cook, J. Non-Cryst. Solids **120**, 152 (1990).